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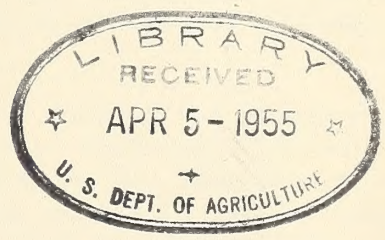
SOLUBILITY CHARTS
FOR
HOMOLOGOUS LONG-CHAIN ORGANIC COMPOUNDS

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A COMPREHENSIVE GRAPHICAL CORRELATION OF
LITERATURE DATA FOR 138 SYSTEMS INVOLVING
11 HOMOLOGOUS SERIES AND 17 SOLVENTS

By

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A COMPREHENSIVE GRAPHICAL CORRELATION OF LITERATURE DATA FOR 138 SYSTEMS INVOLVING 11 HOMOLOGOUS SERIES AND 17 SOLVENTS

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The charts here presented constitute a comprehensive critical review of the published solubility data for 138 systems involving 11 homologous series and 17 different solvents. Most of them were constructed in connection with the preparation of a recent publication (1) from this Laboratory in which it was demonstrated that such plots have a number of important applications in connection with data on the solubilities of members of homologous series. They can be used (A) to smooth out the experimental solubility data, (B) to locate discrepancies caused by experimental error or by an impurity in one sample in the series, and (C) to predict by graphical interpolation or extrapolation the solubility of missing members of the series.

Because of space limitations, only four of the charts were included in the publication to illustrate these applications. Since they show at a glance the agreement between the available solubility data for the members of each homologous series in each solvent and since they supply for each specific system considerable practical information not included in the journal article (1) and not otherwise obtainable, all of these charts are now being made available.

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The following discussion of the theoretical basis and applications of these charts incorporates a summary of the previous publication (1) to which the reader is referred for greater detail.

From the approximate freezing-point-lowering equation and the known empirical relationships between the number of carbon atoms, n , and the heats and entropies of fusion of the members of a homologous series the following linear equation has been derived:

$$\log N = a + bn \quad (1)$$

in which N is the solubility of the homologues (expressed in mole fraction) in a given solvent at a given temperature and a and b are constants depending upon the temperature and the systems involved. If the relationships upon which equation 1 is based were valid, a straight line would be obtained for each temperature by plotting $\log N$ vs. n . Actually they are not strictly valid and therefore the experimental solubilities would not necessarily be expected to conform to the straight-line relationship of equation 1. However, since the deviations would in all probability vary regularly as the chain length increases in a homologous series the $\log N$ vs. n curves (isotherms) would be expected to be smooth.

This method of plotting was applied to the extensive data published by Ralston, Harwood, Hoerr, and coworkers, who have made careful systematic studies of the solubility of the homologous fatty acids (2,3), methyl esters of the fatty acids (4), primary amines (5), symmetrical secondary amines (6), primary alcohols (7), symmetrical ketones (8), nitriles (9), amides (10), anilides (10), N,N-diphenylamides (10), and esters of stearic acid (4), in such solvents as benzene, cyclohexane, carbon tetrachloride, chloroform, ethyl ether, glacial acetic acid, ethyl acetate, butyl acetate, acetone, butanone, methanol, 95% ethanol, isopropanol, *n*-butanol, nitroethane, acetonitrile, and water. All of the solubilities were at temperatures below the melting point of the compounds except for a few values with water as the solvent.

The data were plotted on semi-logarithmic coordinates as solubility in mole % (100 N) against the total number of carbon atoms, usually at temperature intervals of 10° C. Solubilities of less than 0.1% were not considered unless reported to a sufficient number of significant figures to ensure the desired precision. Smooth curves were obtained as expected except for the normal aliphatic amides, which show anomalies in their melting points as well, and which have therefore not been included. Each of the 138 resulting charts consisted of a family of isotherms representing the solubilities of the members of a given homologous series in a given solvent.

APPLICATIONS

Because they are known to be smooth curves these $\log N$ vs. n plots have a number of important applications in connection with data on the solubilities of members of a homologous series:

Smoothing of experimental solubility data. The experimental solubility data considered (2-10) were obtained by the typical procedure of determining the solubility temperatures of a limited number of compositions, drawing a curve through the experimental points, and then tabulating the solubilities at selected temperatures (in this case at ten-degree intervals) as read by graphical interpolation from this solubility curve. Even with perfect data the accuracy of these interpolated solubilities is limited; the experimental points do not define the solubility curve precisely, especially if they are far apart and if there is much curvature. Here the $\log N$ vs. n plots can be used to advantage as a guide. The solubility curves for the individual members of the series should be smoothed or adjusted so that in addition to satisfying the experimental solubilities for the individual compounds they also result in smooth $\log N$ vs. n isotherms for the whole series. Unfortunately this procedure can not readily be demonstrated with the solubility data here considered; only the interpolated values at ten-degree intervals were reported, the original experimental data being represented only graphically on small-scale plots which would require reproduction on a magnified scale to permit the experimental solubilities to be read off with sufficient accuracy.

Detecting discrepancies. In some cases it may be found that one or two points in a system of $\log N$ vs. n isotherms fall considerably above or below the curves established by the other points. Consider, for example, the point representing the solubility of myristic acid ($n = 14$) in butanone, at 20° C., which falls below the 20° isotherm (Chart 9). Since all of the other isotherms in this system are straight lines the 20° isotherm would certainly be expected to be straight and is defined by the four other points as plotted. It seemed probable therefore that the solubility of myristic acid in butanone at 20° C. should be about 6.7 instead of 5.5 mole % as reported. This was confirmed by determining the solubility temperature of a 6.31 mole % mixture of pure myristic acid and purified butanone. The acid was completely dissolved at $18.9^\circ \pm 0.2^\circ$ C. Similarly the solubility of myristic acid in absolute methanol was determined and found to be 2.99 mole % at $20.4 \pm 0.2^\circ$ C., which is in better agreement with the smoothed isotherm for the system than the reported value of 2.37 mole % at 20° C. (Chart 10). In the same system the reported solubilities of myristic acid at 10° C. and of lauric acid ($n = 12$) at 0° C. appear to be too low.

To mention a few more examples, the isotherms for the primary alcohols in ethyl ether (Chart 71) would indicate that the solubility of *n*-hexadecanol ($n = 16$) should be about 0.65 instead of 0.91 mole % at 0° C. Similarly, judging from the isotherms for the fatty acid series in ethyl acetate (Chart 6), the solubility of lauric acid ($n = 12$) in this solvent at 30° C. should be about 38 instead of 52.4 mole % as reported and that for capric acid ($n = 10$) at 10° C. should be about 25 instead of 31.5 mole %.

It is not unlikely that some of these apparent discrepancies can be attributed to unavoidable inaccuracies in drawing the basic smooth solubility curves through the original experimental points. In other words, much better agreement might have been obtained by using the above-mentioned procedure for smoothing the experimental data.

It will be noted that the solubilities for the C₃₀ member of the series of symmetrical secondary amines in chloroform (Chart 58) tend to be more or less consistently higher than would be expected from the isotherms. This behavior could be explained by the presence of a slight impurity in this sample.

Predicting solubilities of missing members of a homologous series by interpolation or extrapolation. The log *N* vs. *n* plots can be used to estimate with some precision the solubilities of missing members of a homologous series, the precision depending upon the accuracy and consistency of the original data, and upon the slope and the amount and type of curvature of the isotherms. Thus the published solubility data for the homologous symmetrical aliphatic secondary amines include only the members having the following total number of carbon atoms: 16, 24, 26, 28, 30, and 36. From the smooth log *N* vs. *n* isotherms (Charts 55 - 66) it is possible by graphical interpolation to read off the solubilities of the missing members of the series at various temperatures for each solvent; i.e., those members containing 18, 20, 22, 32, and 34 carbon atoms (1). By extrapolation the solubilities for the C₃₈ and, in a few instances, for the C₁₄ member can also be estimated. Similarly, since the solubility data for the anilides and the *N,N*-diphenylamides include only the capric, lauric, palmitic, and stearic acid derivatives (Charts 107 - 132), it is possible to estimate the probable solubilities of the missing member of each of these series, myristanilide and *N,N*-diphenylmyristamide, over a range of temperatures in thirteen solvents (1).

The probable accuracy of the solubility values obtained by interpolation or extrapolation varies with the system and particularly with the extent to which the specific isotherms are defined by the experimental points. Consider, for example, the solubilities of the

symmetrical secondary amines in carbon tetrachloride (Chart 57). The interpolated values for the C_{32} and C_{34} amines at 40° and 50° C. would be expected to be quite accurate. That for the C_{20} amine at 10° C. and the extrapolated values for the C_{38} amine at 40° and 50° C. are less reliable but probably more so than the extrapolated values for the C_{20} amine at 30° C. and for the C_{40} amine at 40° and 50° C. In general, solubility values obtained by extrapolation are less trustworthy than interpolated values, especially when the isotherms are not straight lines.

Alternation occurs in the melting point and heat of fusion in the fatty acid series and therefore, as would be expected, the $\log N$ vs. n isotherms for the odd-membered acids are quite distinct from those for the even acids. It is thus impossible to estimate the solubility of the odd acids by interpolation in the isotherms for the even acids and vice versa. The same is probably true for any homologous series showing alternation of melting point. Only the solubility data for methyl tridecanoate ($n = 14$) in four different solvents are available to test this point and in every instance the points fail to fall on the $\log N$ vs. n isotherms for the members of the series for which n is odd.

It seems reasonable to assume that for a homologous series such as the primary alcohols, which shows no alternating effect in the melting point (11), the isotherms for the odd and even members would coincide and that therefore it should be possible to predict the solubilities of the missing (odd) members by interpolation in the $\log N$ vs. n plots of this alcohol series for the various solvents (Charts 67 to 79). Similarly, by analogy to the symmetrical secondary amines (Charts 55 to 66), it might be assumed that the solubilities of the symmetrical ketones having 21, 25, 29, and 33 carbon atoms could be predicted by interpolation in the $\log N$ vs. n plots for those having 23, 27, 31, and 35 carbon atoms, shown for the various solvents in Charts 80 to 91. In such cases, however, the basic assumption should first be confirmed by determining at least one solubility curve for one of the missing members of the homologous series in question.

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